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NEW MATERIALS FOR INFRARED TRANSMITTING ELECTROOPTIC FILTERS

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Hughes Research Laboratories
3011 Malibu Canyon Road
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During the last quarter, GeS_2 was grown as small single-crystal samples and evaluated. Over the range from 5 kHz to 100 kHz, the dielectric constant shows little variation: 10.73 at 5 kHz, 10.52 at 100 kHz. Far infrared spectroscopy measurements in regions where the dielectric constant ϵ is essentially equal to the square of the refractive index, $\epsilon = n^2$, are in generally good agreement with the above measurements, taking into account some of the features of the curve of ϵ as a function of frequency.

Initial runs to synthesize ZnIn_2S_4 yielded primarily $\text{Zn}_3\text{In}_2\text{S}_6$ with little transport of ZnIn_2S_4 . The iodine-transport technique showed little transport in all runs, but CdIn_2S_4 was formed from the constituent binary compounds, CdS and In_2S_3 , by a sintering-recrystallization process. Additional binary components were synthesized during the quarter to facilitate subsequent growth of the ternary compounds of interest.

A general-purpose portable electrical test fixture was fabricated which is capable of measuring:

- Dielectric constant and dissipation
- Resistivity (by Van der Pauw four-point probe method)
- Dielectric breakdown
- Electrooptic coefficient

at temperatures in the range from 77°K to 600°K and at vacuum to 10^{-7} Torr.

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REPORT SUMMARY

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The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those most likely to have an EO coefficient an order of magnitude higher than materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently. Our approach will overcome these obstacles by first synthesizing 20 polycrystalline samples; subsequently, dielectric constants at low and ambient temperatures will be determined and the two best materials of the survey will be grown as single crystals (second year of the program).

During the last quarter, GeS_2 was grown as small single-crystal samples and evaluated. Over the range 5 kHz to 100 kHz, the dielectric constant shows little variation; 10.73 at 5 kHz, 10.52 at 100 kHz. Far infrared spectroscopy measurements in regions where the dielectric constant ϵ is essentially equal to the square of the refractive index,

$$\epsilon = n^2,$$

$n^2 \approx \epsilon$

are in generally good agreement with the above measurements, taking into account some of the features of the curve of ϵ as a function of frequency.

Initial runs to synthesize ZnIn_2S_4 yielded primarily $\text{Zn}_3\text{In}_2\text{S}_6$ with insignificant transport of ZnIn_2S_4 . The iodine-transport technique showed little transport in all runs, but CdIn_2S_4 was formed from the constituent binary compounds, CdS and In_2S_3 , by a sintering-recrystallization process.

Additional binary component compounds were synthesized during the quarter to facilitate subsequent growth of the ternary compounds of interest.

A general-purpose portable electrical test fixture was fabricated which is capable of the following measurements:

- Dielectric constant and dissipation
- Resistivity (by Van der Pauw four-point probe method)
- Dielectric breakdown
- Electrooptic coefficient

at temperatures in the range from 77°K to 600°K and at vacuum to 10^{-7} Torr.

SECTION 1

INTRODUCTION AND SUMMARY

A. PROGRAM OBJECTIVES

The objectives of this program are to find and develop new IR transmitting materials and to provide new data on the electrooptic (EO) properties of those materials most likely to have EO coefficients an order of magnitude higher than those of the materials currently in development for tunable filters. The main technical problems anticipated include the synthesis and single-crystal growth of these materials: many are poorly characterized and others have high melting points or melt incongruently. Our approach will overcome these obstacles. First, we will synthesize 20 polycrystalline samples. Then the dielectric constant of each, at both low and ambient temperatures, will be determined, and the two best materials of the survey will be grown as single crystals (second year of the program).

B. SUMMARY

During the last quarter, GeS_2 was grown as small single-crystal samples and evaluated. Over the range from 5 kHz to 100 kHz, the dielectric constant varied little: it was 10.73 at 5 kHz and 10.52 at 100 kHz. Far infrared spectroscopy measurements in regions where the dielectric constant ϵ is essentially equal to the square of the refractive index,

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technique showed little transport in all runs, but CdIn_2S_4 was formed from the constituent binary compounds, CdS and In_2S_3 , by a sintering-recrystallization process. Additional binary components were synthesized during the quarter to facilitate subsequent growth of the ternary compounds of interest. A general-purpose portable electrical test fixture was fabricated that is capable of measuring:

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- Resistivity (by Van der Pauw four-point probe method)
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SECTION 2

MATERIALS PREPARATION

A. GROWTH OF GERMANIUM SULFIDE CRYSTALS

Two approaches were taken to growing crystals of GeS_2 : sublimation and the Bridgman technique. In the preparation of GeS_2 by direct reaction of the elements, the GeS_2 sublimed readily. This presented the possibility that GeS_2 could be grown by sublimation. The compound was encapsulated under vacuum into a 1-cm (i.d.) tube, 20 cm in length, and placed in a furnace with a flat profile at 700°C . The tube was pulled through the profile at a rate of 0.1 cm/hr for 15 days. No sublimation took place. The material was solid and polycrystalline.

The melting point of GeS_2 has been reported¹ as 740°C , and information could be found on the vapor pressure of GeS_2 at any temperature. Since the compound was observed to sublime and possibly to decompose at high temperatures, attempts at Bridgman growth would increase the possibility of an explosion due to excessively high vapor pressures. The Bridgman method was tried in a furnace set at 850°C . The rate of growth was 2 mm/hr. The run was taken out of the furnace hot before the last remaining liquid had frozen. A dark brown vapor was observed above the compound, indicating a sulfur pressure over the melt and hence some decomposition. The result was a crystalline yellowish material identified as GeS_2 by X-ray diffraction (Figure 1), from which single-crystal layers could be peeled. An amber-colored amorphous section (the last to freeze) was also identified as GeS_2 by microprobe analysis.

B. PREPARATION OF BINARY CHALCOGENIDES

Mixtures of binary chalcogenides can be used as source material in the gas transport reaction method to synthesize ternary compound crystals. We have pursued the preparation of ZnS , CdS , CdSe , CdTe ,

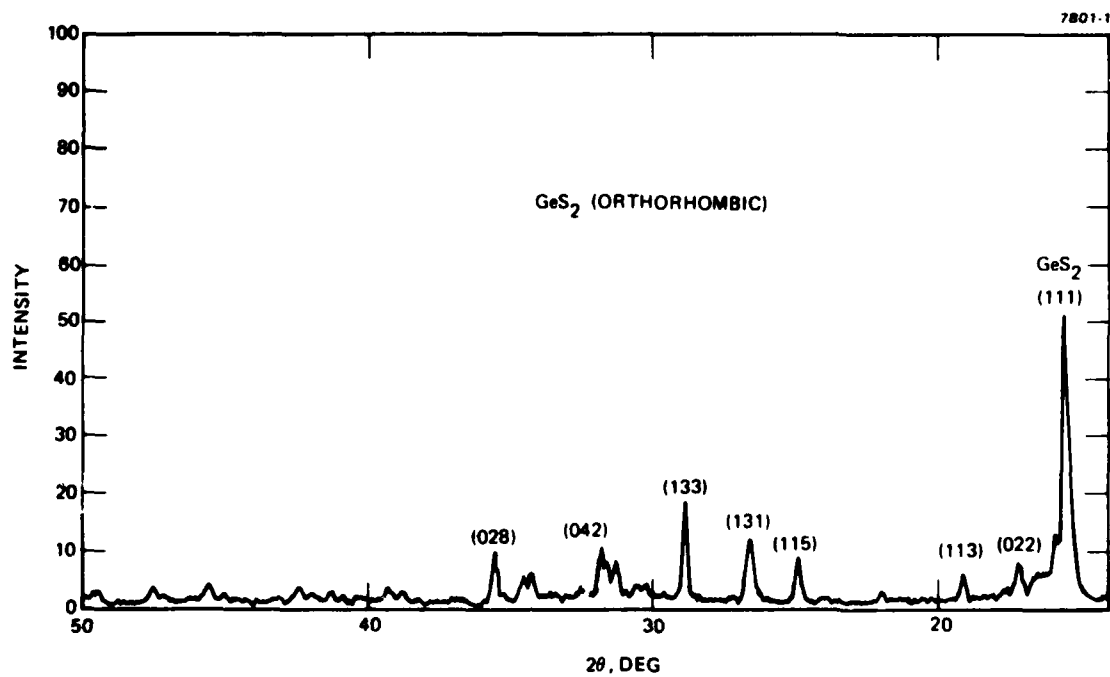
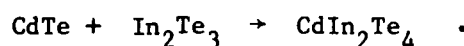
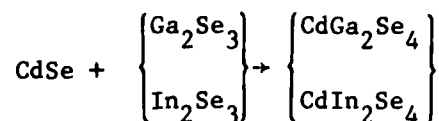
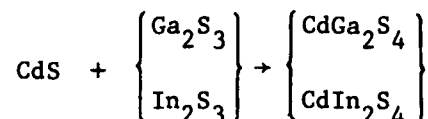
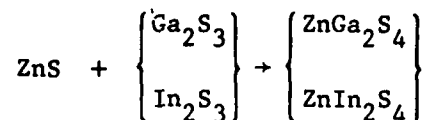


Figure 1. X-ray diffraction pattern (indexed) of GeS₂.

In_2Se_3 , Ga_2S_3 , In_2S_3 , Ga_2Se_3 , and In_2Te_3 . We are now investigating the synthesis of the following ternary compounds by the following reactions:



Electronic-grade powders purchased commercially are used as the sources of ZnS, CdS, and CdSe. These powders are sublimed under dynamic vacuum (Figure 2) to purify them before they are used for synthesizing the ternary compound. Fused silica ampoules are loaded with about 250 g of the chalcogenides and inserted slowly into the hot furnace while under vacuum. When the tube is in the flat portion of the thermal profile, and the furnace has reached operating temperature, the tube is slowly withdrawn from the furnace. The sublimation temperatures are not critical but are on the order of 1100°C for ZnS, 1000°C for CdS, and 900°C for CdSe.

Indium selenide was prepared by reaction of the elements in an evacuated tube (Figure 3). Indium is placed in a boat within a sealed evacuated ampoule with selenium at the cool end of the ampoule. The ampoule is inserted slowly into a hot furnace (its temperature is set above the melting point of the compound). The reaction of selenium with indium proceeds slowly, thereby reducing the danger of an uncontrolled exothermic reaction. After the reaction is completed, the furnace is turned off with the compound still inside and allowed to cool to room temperature.

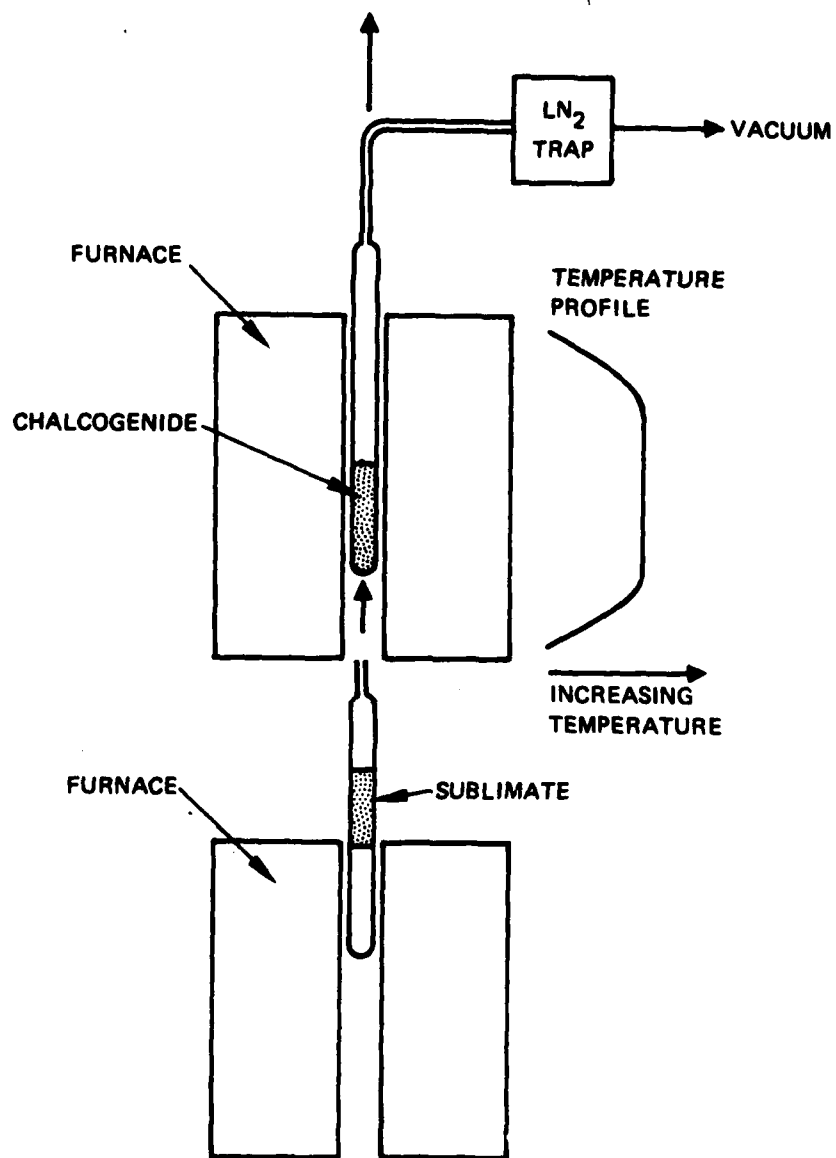


Figure 2. Sublimation-purification process.

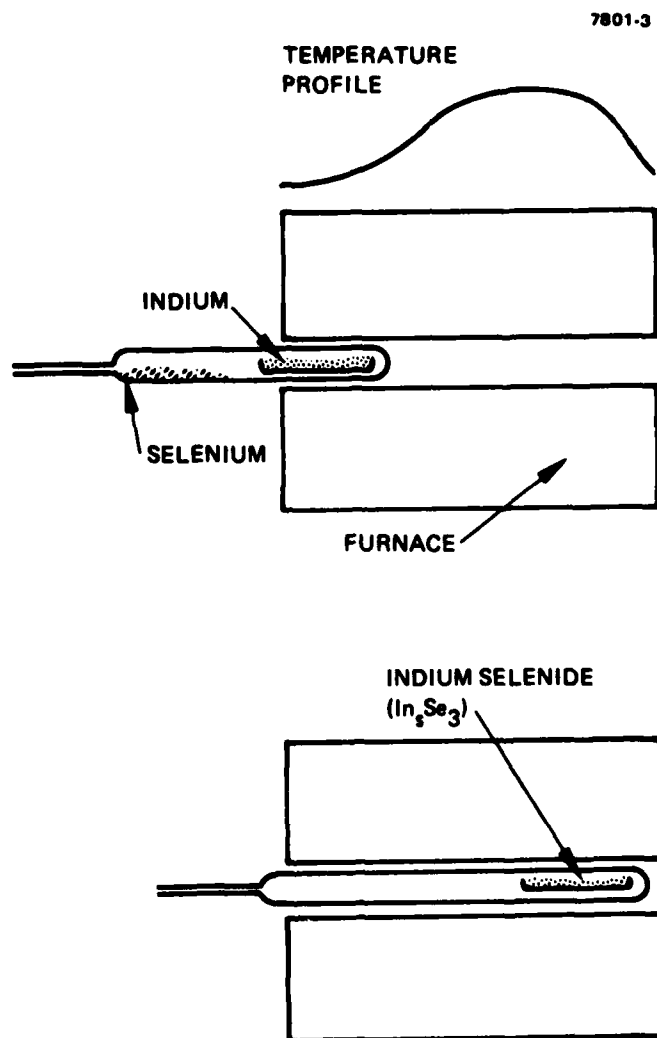


Figure 3. Preparation of In_2Se_3 .

C. PREPARATION OF LiGaS_2

Because Li_2S is deliquescent and highly reactive to water in the atmosphere, the ternary chalcogenide LiGaS_2 was prepared by reaction of H_2S with LiGaO_2 rather than with the binary compounds Li_2S and Ga_2S_3 . Gallium metal was first dissolved in 15 N HNO_3 . After complete dissolution, a stoichiometric amount of LiNO_3 was added. The mixture was evaporated to dryness on a hot plate to obtain $\text{LiGa}(\text{NO}_3)_4$. This material was transferred into a fused silica boat in a fused silica ampoule.

Since the physical and chemical properties of LiGaS_2 are not reported in the handbooks, the preparation had to be carried out cautiously; a great part of it depended on observation. Also, as a safety precaution because the reaction involved H_2S , the reaction was restricted to the working day. The set-up was heated slowly to approximately 600°C under N_2 to decompose the nitrate to the oxide. When brown fumes of nitrogen oxide were no longer visible, the temperature was raised to $\approx 800^\circ\text{C}$ over a period of 4 hr under H_2S . Emerging H_2S gas flowed into an outlet connected to two bubblers containing NH_4OH ; these acted as H_2S traps. X-ray diffraction showed that the material was mostly LiGaO_2 .

The LiGaO_2 was ground and reheated to 1000°C for 2 hr. This time, the material was heterogeneous: colored pink and white. X-ray analysis of both phases gave the same lines, but the pink phase had better defined lines and the LiGaO_2 lines were not as intense. There were other lines present and these could not be identified. (There is no ASTM index card for LiGaS_2 .) These lines could not be attributed to Li_2S , Ga_2S_3 , LiGa silicates, Li silicates, or Ga oxides.

The material was ground again and then reheated to 1000°C for 3 hr in H_2S and N_2 . Melting was observed. X-ray analysis showed the same lines as during the previous run. Since there was some attack on the material (probably due to the Li_2O), the run was repeated using a graphite ampoule at 1000°C for 3 hr under H_2S and N_2 . The final product, which is believed to be mostly LiGaS_2 , is being chemically evaluated. Crystal synthesis experiments will be made during the next quarter.

D. PREPARATION OF TERNARY COMPOUNDS BY CHEMICAL VAPOR TRANSPORT

Chemical vapor transport (CVT) is a useful technique for materials that have a high melting point, dissociate at the melting point, or melt under elevated pressures. By using CVT, lower temperatures can be used since the volatile intermediate phases have higher vapor pressures relative to the material of interest. In addition, this method allows separation of phases since the solid condenses within the section of the container that is at the proper temperature. Compounds that melt incongruently (i.e., with decomposition) can also be synthesized since the growth takes place at temperatures below the melting point of the compound. The defect chalcopyrites of the type $A^{II}B_2^{III}C_4^{VI}$ fall into this category.

The mass transport rate is a function of:

- Tube geometry. Increasing the cross section of the tube increases the rate (which is controlled by thermal convective processes); increasing the length of the tube slows down the rate of transport.
- The concentration of the transport. At low concentrations, the rate is slow. As the concentration is increased, the rate increases, slowly at first and then more rapidly.
- The average temperature and the temperature difference (ΔT) between the source material and the growing crystal. However, the temperature difference will be of minor importance when thermal convective processes are dominant. Higher temperatures increase both vapor concentration and convection, as discussed above. A greater thermal differential increases the transport rate since vapor pressure will tend to equilibrate to the temperature at the source, while condensation occurs in the cooler zone.

E. $ZnIn_2S_4$ AND $CdIn_2S_4$

The CVT method using iodine as transport medium was employed to grow $ZnIn_2S_4$ and $CdIn_2S_4$. Two tube sizes were used for growing these compounds: each had a 1-cm i.d.; one was 20 cm long and the other was

33 cm long. The 20-cm tubes were pulled through a sloping temperature gradient, while the 33-cm tubes were placed in a thermal gradient and remained stationary. A sloping gradient is useful along the crystallization tube to find the optimal temperature for crystal deposition. The tubes, which contained approximately 25 g of crystal source material, were loaded with iodine in various amounts and sealed off under vacuum. To prevent the iodine from subliming, the tube was immersed in liquid nitrogen during evacuation.

Five runs were made to grow ZnIn_2S_4 . Three of the runs consisted of pulling the tube through the temperature gradient from 930°C to 700°C at a speed of 2 mm/hr. In the first run the tube exploded. The other two runs were completed without incident. The final two runs of the five were done in situ. The tubes were loaded as before with equal molar amounts of ZnS and In_2S_3 , iodine was introduced, and the tube was evacuated and sealed. These tubes were placed in a temperature gradient of 1000°C to 700°C. The growth time for each was approximately 150 hr. The concentration of iodine ranged from 0.6 to 6 mg/cm³ of tube volume.

In all cases, there was insignificant transport. We identified $\text{Zn}_3\text{In}_2\text{S}_6$ by X-ray analysis (Figure 4) as the resulting compound that dominated in all the runs. A small amount of transported material was identified as ZnIn_2S_4 (Figure 5). The bulk of the material sintered and underwent grain growth. This was the material primarily identified as $\text{Zn}_3\text{In}_2\text{S}_6$.

Equal molar amounts of CdS and In_2S_3 along with iodine equivalent to 6 mg/cm³ of tube volume were sealed under vacuum into a 33-cm tube. This tube was placed in a temperature gradient of 1000°C to 700°C. After 150 hr, no significant transport had taken place. The material sintered and underwent grain growth. X-ray diffraction analysis was used to identify it as CdIn_2S_4 (Figure 6). A 1 cm x 2 mm sample has been cut for measurements.

The reason for the lack of transport in the above experiment is not obvious. The tubes are of sufficient diameter and not too long; the sizes are comparable to the sizes reported in the literature. Also,

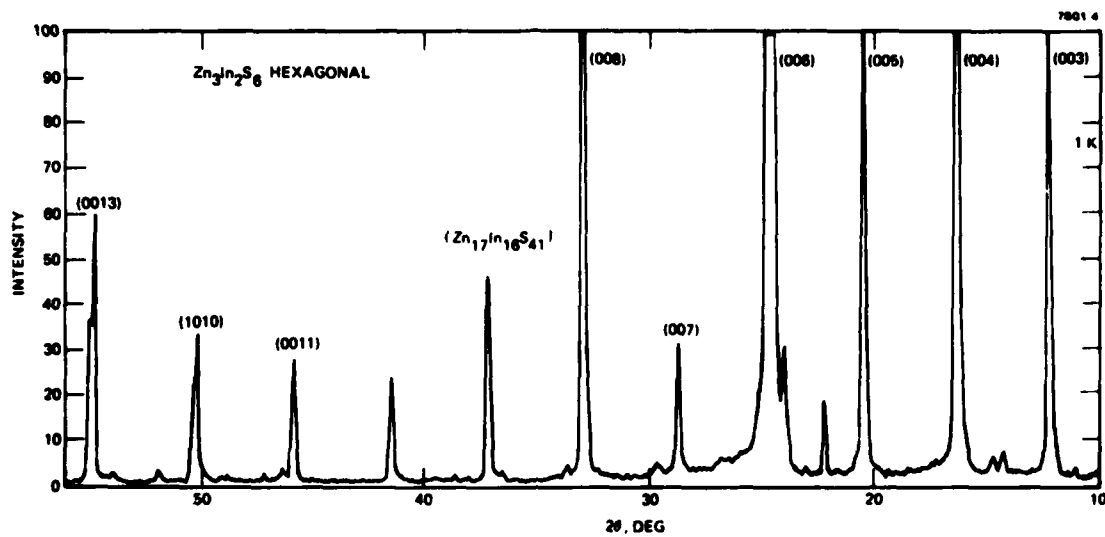


Figure 4. X-ray diffraction pattern of $\text{Zn}_3\text{In}_2\text{S}_6$.

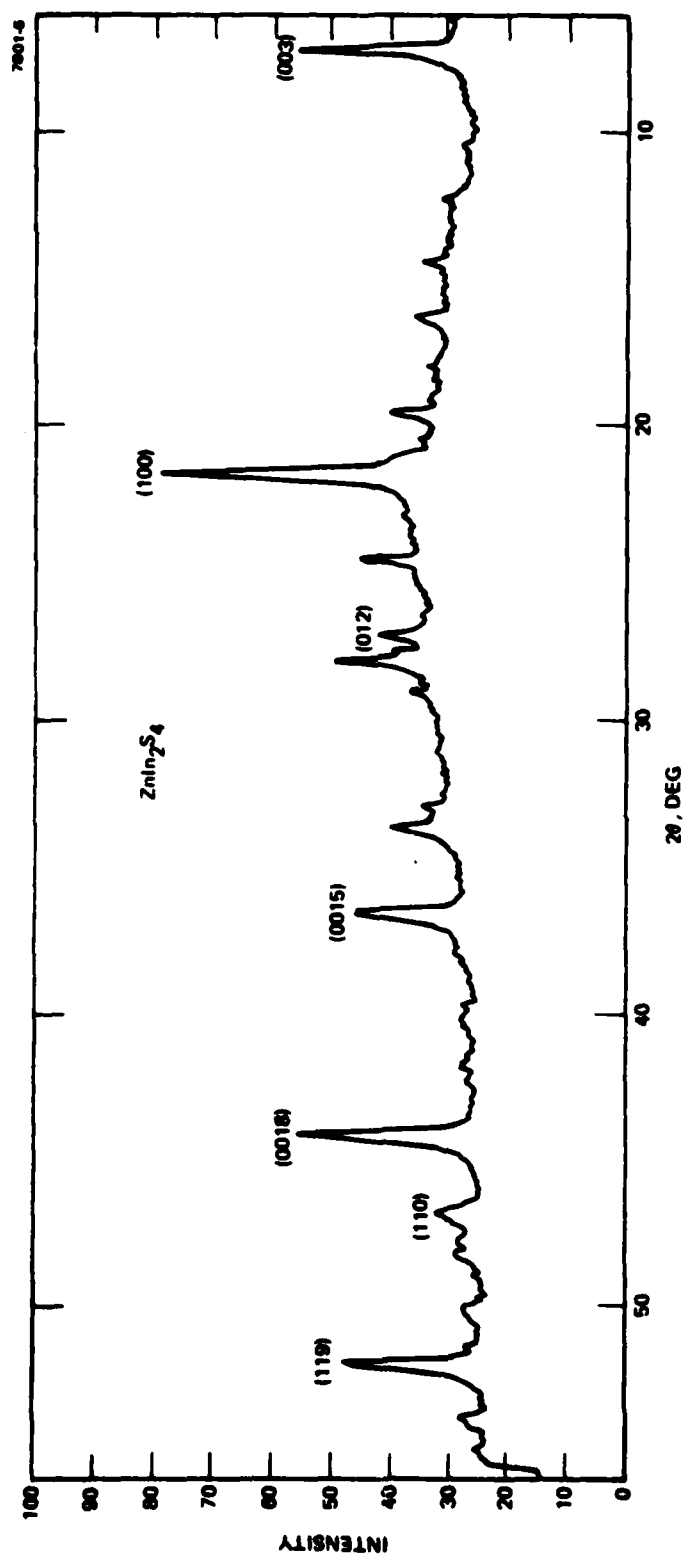


Figure 5. X-ray diffraction pattern of ZnIn₂S₄.

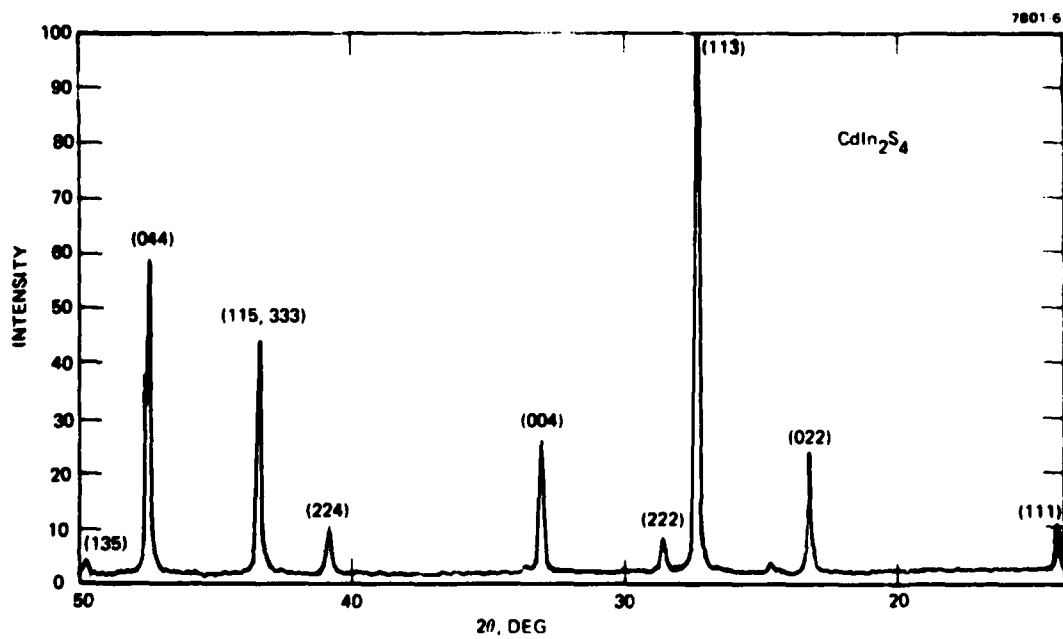
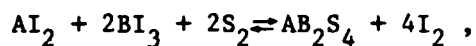


Figure 6. X-ray diffraction pattern of CdIn_2S_4 .

tubes of this size have been used on numerous occasions in this laboratory to grow binary compounds by CVT techniques. The concentration of iodine is sufficient without getting into a dangerous situation of pressure buildup. The temperature difference (ΔT) is large enough for transport even though it may not be operative since convective processes may be dominant. The length of time in the furnace was certainly adequate for transfer to occur. Since the reasons for lack of transport are not clear, we are preparing to evaluate HCl as the transport gas. In addition, we have prepared CdI_2 and ZnI_2 by direct reaction of the elements and plan to use these compounds as intermediaries in the reaction:



where A = Cd, Zn and B = In, Ga. Since these compounds are not as volatile as iodine, the loading procedure is simplified and no precautions are required to prevent loss during evacuation. The diameter of the tubes to be used will be doubled since the transport rate increases exponentially (a power of two) with increased tube diameter.

SECTION 3

MATERIALS EVALUATION

A. DIELECTRIC CONSTANT MEASUREMENTS

Dielectric constant measurements were performed during the last quarter on a GeS_2 crystal. These crystals, shiny white in appearance, cleave very easily on (111) planes. They are also very soft and somewhat difficult to polish mechanically. A small piece of the as-grown boule was cut and then cleaved to yield a test sample with parallel faces. Electrodes were formed by applying silver paint to the parallel faces. The measured thickness of the capacitor was 9.906 mm, and the area of coincidence of the parallel electrodes was 15.6 mm^2 . The capacitance and the dissipation factor of the capacitor were measured as a function of frequency on a Boonton Model 75C direct capacitance bridge. The frequency range was from 5 kHz to 100 kHz. These measurements were performed at room temperature using peak test signal levels of 1 to 3 V.

The static dielectric constant ϵ_s was obtained from the measured capacitance at any given frequency by using the formula:

$$\epsilon_s = \frac{Cd}{8.85 A} ,$$

where d is the thickness of the capacitor (in m), A is the area of coincidence of the electrodes (in m^2), and C is the measured capacitance (in pF). Figure 7 shows that, over the range from 5 kHz to 100 kHz, the change in the dielectric constant is fairly small (10.73 at 5 kHz as compared to 10.52 at 100 kHz). Figure 8 shows the dissipation factor as a function of test frequency. The curve has some interesting features. Two strong primary peaks are seen at 5.5 and 65. kHz; these are followed by a definite, albeit weaker, secondary peak at 45 kHz. These dielectric relaxation peaks suggest separate, distinct relaxation processes and deserve further investigation.

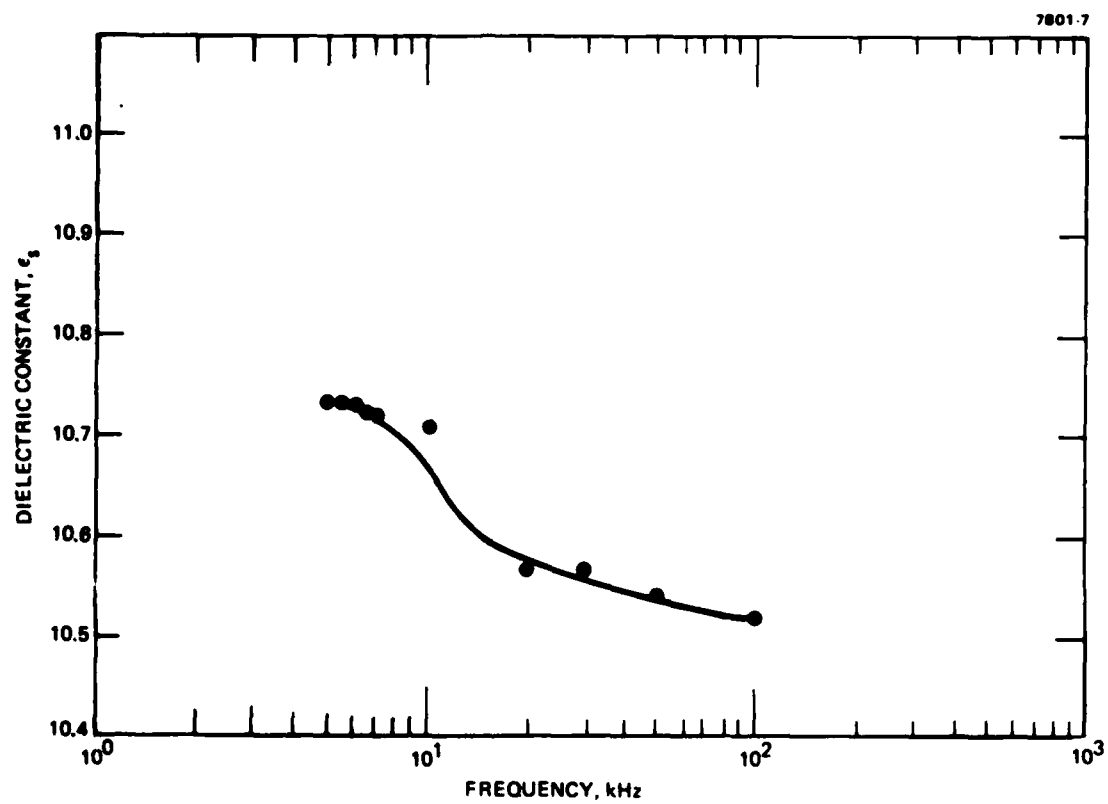


Figure 7. GeS_2 dielectric constant as a function of frequency.

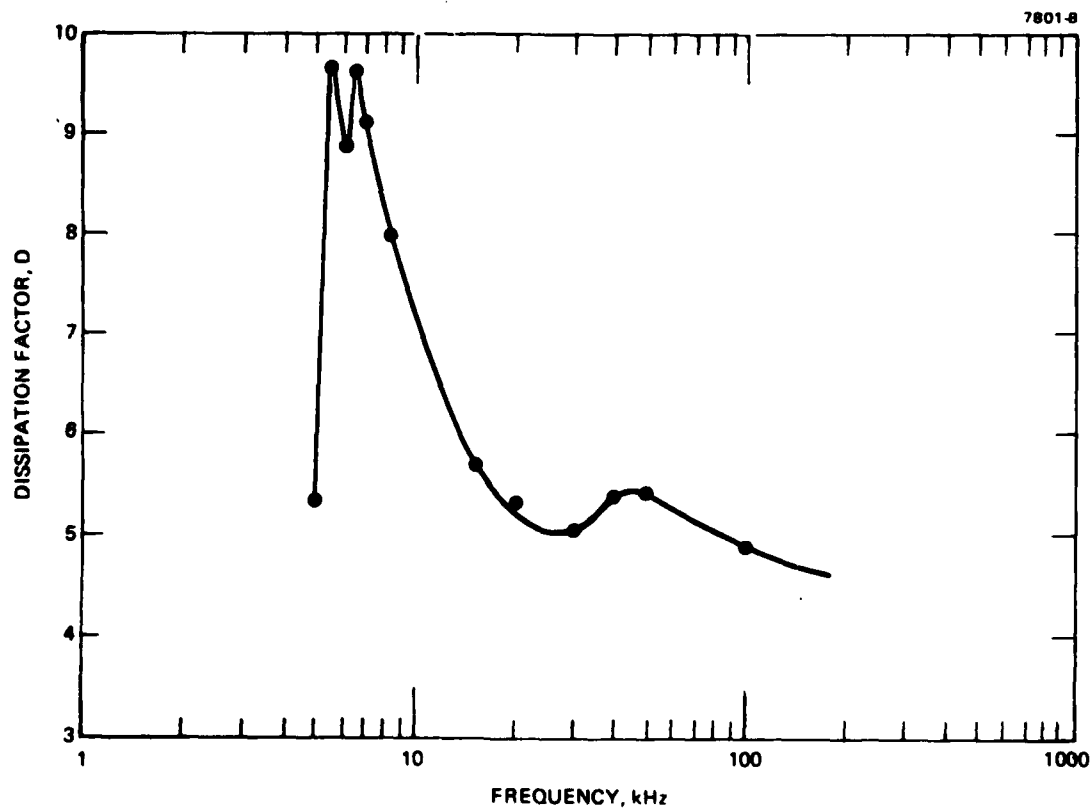


Figure 8. Dissipation factor versus frequency. Sample is GeS_2 .

The data shown in Figures 7 and 8 represent measurements on only one sample. Since the as-grown GeS_2 crystal boule had a small diameter and the crystal tends to cleave easily, it was not possible to obtain a large enough sample on which large-area electrodes could be formed. The small-electrode-area sample discussed above had only a small capacitance (a few pF). Because the capacitance of the test capacitor was so low, accurate measurements of the dielectric constant and dissipation factor were very difficult. We are currently trying to synthesize larger diameter GeS_2 crystals, which would yield larger capacitance (≥ 100 pF) capacitors. Such capacitors could be used to check the reproducibility and accuracy of the dielectric constant and the relaxation measurements.

B. MEASUREMENT APPARATUS

A general-purpose electrical test fixture has just been fabricated. With this portable test fixture, dielectric constant and dissipation resistivity (using Van der Pauw's four-point probe method),² dielectric breakdown, and EO coefficient measurements are possible at any temperature from 77°C to 600°C. In addition, the fixture can be evacuated to 10^{-7} Torr. Figures 9 and 10 show some of the salient features of this facility.

More accurate dielectric constant and relaxation measurements at 77°K and higher temperatures on GeS_2 , as well as additional new ternary chalcopyrite materials, are currently in progress and will be reported in the next quarterly report.

C. FAR INFRARED SPECTROSCOPY - GeS_2

The far infrared transmission spectrum of GeS_2 (Figure 11) was obtained and analyzed under the direction of Professor Paul L. Richards, Department of Physics, University of California at Berkeley. The top curve (curve 1) in Figure 11 shows the transmittance of a GeS_2 sample,

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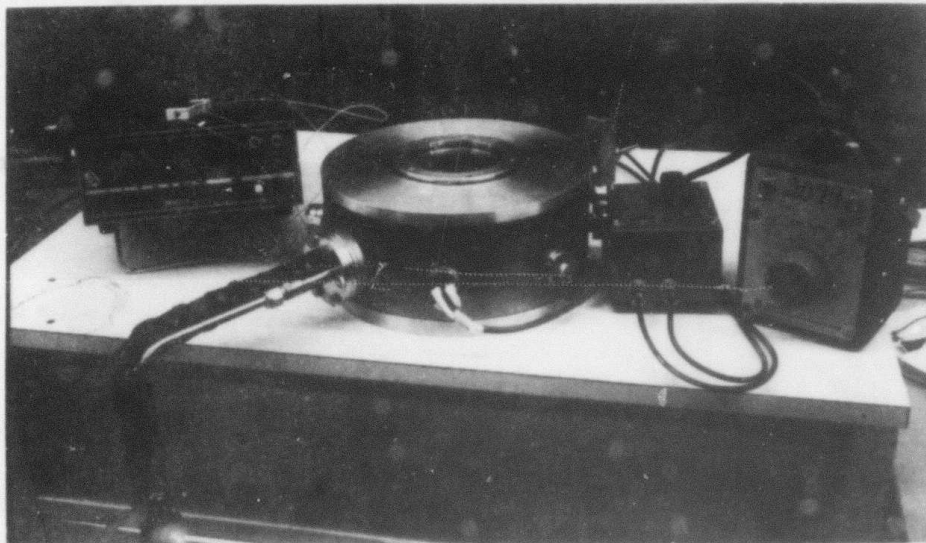


Figure 9. Electrical testing apparatus.

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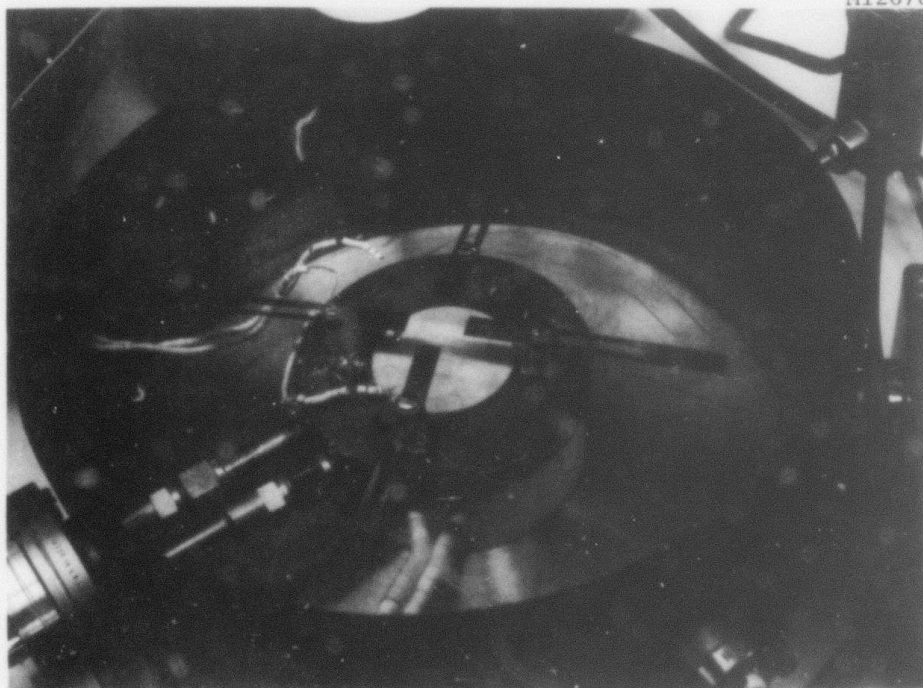


Figure 10. Electrical testing apparatus (internal view).

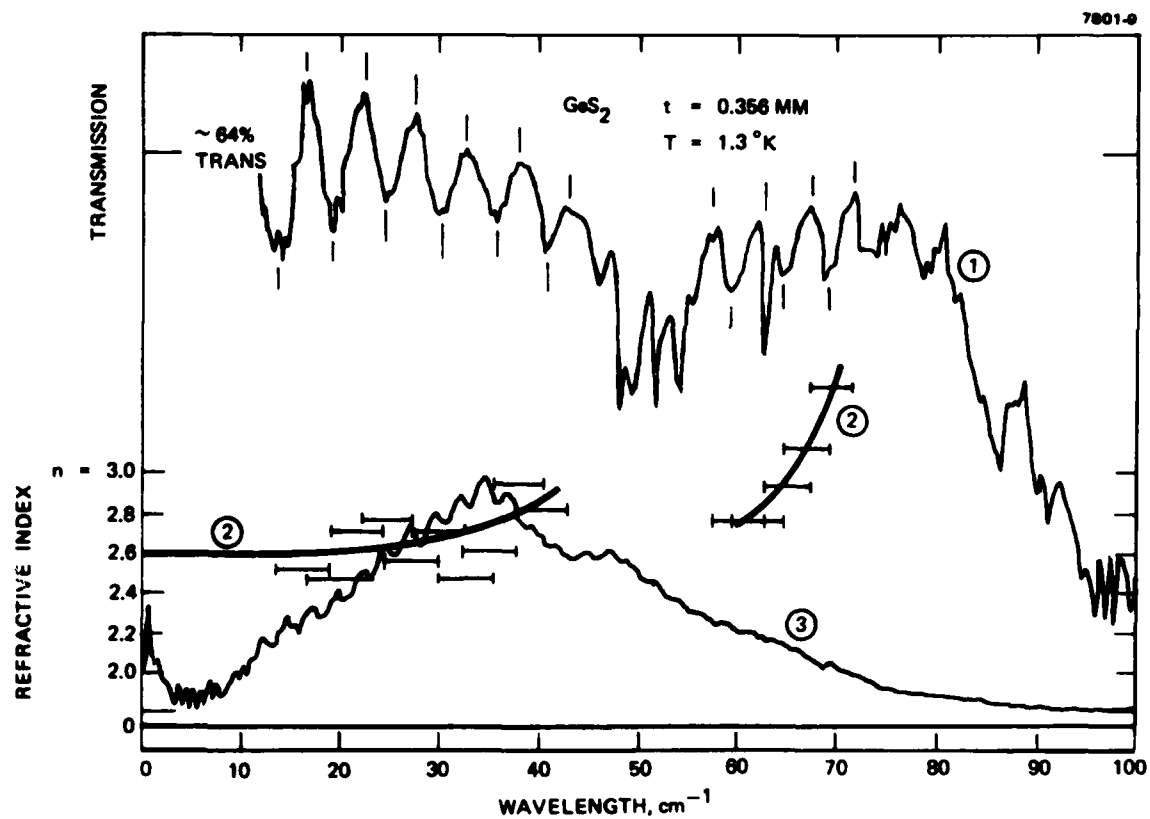


Figure 11. Far IR transmission of GeS₂ (Curve 1). Index of refraction of GeS₂ as a function of wavelength (Curve 2). Curve 3 is empty sample cell.

0.356 mm thick in the range of 10 to 80 cm^{-1} at a temperature of 1.3°K. The spectrum shows interference fringes and sharp absorptions at 48 to 63 cm^{-1} . The index of refraction was estimated from the known mechanical thickness t and the observed wavelengths of the maximum and minimum in transmission:

$$\lambda_{\text{max}} = \frac{2n(\lambda)t}{m}$$

$$\lambda_{\text{min}} = \frac{4n(\lambda)t}{2m + 1} ,$$

where m is any integer ≥ 1 . These equations are applied in the spectral regions where the complex part of the index is negligible. Curve 2 indicates the estimated index of refraction. At these frequencies, the dielectric constant is equal to the index of refraction squared:

$$\epsilon = n^2 .$$

The dispersion due to the 48 to 63 cm^{-1} modes and also to higher frequency modes shows clearly in the diagram.

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